Ne_N-coronene clusters at low temperatures: application and assessment of the Feynman-Hibbs approach

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Feynman-Hibbs (FH) effective potentials allow us to easily include quantum corrections within standard classical simulations of many-body systems at thermal equilibrium. This formulation is increasingly being applied to studies of adsorption of molecular gases in microporous materials[1]. Although the validity of this approach for homogeneous systems has been investigated in detail[2], specific tests for fluid-solid mixtures are scarcer.

We have applied the FH formulation to the study of Ne_N-coronene clusters (N = 1-4, 14) in the 2-14 K temperature range[3], as a prototype for the adsorption of small molecules in carbonaceous substrates. Reliable Ne-Ne and Ne-coronene[4] pairwise potentials are employed using analytical expressions. As in a recent study of He_N-coronene clusters[5], minimum energies of the bare interaction potential are obtained by means of a basin-hopping (BH) approach and the optimized structures are then used as seeds for classical and path-integral Monte Carlo computations (CMC and PIMC). FH potentials are derived both at quadratic (FH2) and quartic (FH4) orders and employed in additional BH and CMC calculations at each temperature. FH2 and FH4 cluster energies and structures are reported and compared with the benchmark PIMC calculations.

For temperatures $T > 4$ K, both FH2 and FH4 potentials are able to correct the purely classical calculations in a consistent way. At lower temperatures, where zero-point energy dominates over thermal effects, the present approach fails, especially the FH4 potentials. It is thus crucial to apply the quartic corrections (recently employed in the diffusion of molecules in nanoporous materials) with extreme caution. A simple model of N classical harmonic oscillators allows us to propose a means of estimating the cut-off temperature for the validity of the method, which is found to increase with the number of atoms adsorbed on the coronene molecule.

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